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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention]This invention relates to the nonaqueous electrolyte which has a overcharge preventive effect and was excellent in the high temperature conservation characteristic, and the lithium secondary battery excellent in the safety at the time of the overcharge using it.

[0002]

[Background of the Invention]The cell using nonaqueous electrolyte is high tension, and has high energy density.

Since reliability, such as keeping, is high, it is widely used as a power supply of consumer electronics.

[0003]Such a cell is manufactured also as a rechargeable battery and the example of representation is a rechargeable lithium-ion battery. This cell comprises an anode which contains occlusion and the active material which can be emitted for lithium, a cathode containing the multiple oxide of lithium and a transition metal, an electrolysis solution, etc. In an electrolysis solution, high permittivity carbonate solvents, such as propylene carbonate and ethylene carbonate, The solution which mixed lithium electrolytes, such as LiBF₄ and LiPF₆, is used for the mixed solvent with hypoviscosity carbonate solvents, such as diethyl carbonate, methylethyl carbonate, and dimethyl carbonate.

[0004]By the way, it is reported that the thermal stability of a rechargeable lithium-ion battery relates to the charging state of a cell. If a cell is charged more than a specified voltage value (i.e., if it overcharges), on an anode, metal lithium will deposit, or the oxidizing degree of a cathode will increase, a chemical reaction with an electrolysis solution will occur easily, and the thermal stability of a cell will fall. Since it is possible that thermal run-away happens the cell by which thermal stability fell by a self-exoergic reaction also under high temperature service, it is important not to make a cell overcharge.

[0005]So, in JP,H9-171840,A, JP,2000-58116,A, and JP,2001-15155,A, use of the electrolysis solution which added biphenyls and alkylbenzenes is proposed. The alkyl compound replaced with two aromatic groups and fluorine atom substituted aromatic compounds are proposed by JP,H11-162512,A as a overcharge inhibitor by which the elevated-temperature characteristic was improved.

[0006]Since biphenyls, alkylbenzenes, and the alkyl compound replaced with the aromatic group and fluorine atom substituted aromatic compounds have low oxidation potential compared with the common

solvent used for a lithium cell, the electrolysis solution which added these becomes that it is easy to be electrolyzed. For this reason, since an electrolysis solution is electrolyzed instead of a cell overcharging, it is effective in preventing a surcharge. Henceforth, the compound which has such a function is called a overcharge inhibitor.

[0007]On the other hand, since a overcharge inhibitor has low oxidation potential, electrolysis may take place despite a small quantity also on condition of an elevated temperature in the anticipated-use state, and a high temperature conservation characteristic may fall. That is, in the electrolysis solution which added the overcharge inhibitor, a overcharge prevention operation and a high temperature conservation characteristic have a relation of a trade-off.

[0008]For example, according to this invention persons' examination, the influence which exerts the above mentioned biphenyls and alkylbenzenes on the battery characteristic in a room temperature is small, but if a not less than 85 ** elevated temperature is used on the voltage of 4.2V, the experimental result to which a battery characteristic falls substantially is obtained. According to this invention persons' examination, as for fluorine atom substituted aromatic compounds, although the high temperature conservation characteristic has been improved a little as compared with biphenyl, the experimental result to which a prevention operation of a surcharge becomes low is obtained, for example. Since oxidation potential is a little higher than biphenyls and alkylbenzenes, although fluorine atom substituted aromatic compounds becomes [the electrolysis under high temperature service] difficult to take place, also when a cell is made an overcharging condition, electrolysis becomes difficult to take place, and this is considered that the prevention operation of the surcharge became low.

[0009]JP,H11-162512,A is describing that 2.5 weight % is enough as the addition of fluorine atom substituted aromatic compounds. However, according to this invention persons' examination, as mentioned above fluorine atom substituted aromatic compounds. Since the prevention operation of a surcharge is a little low as compared with biphenyl, in order to improve the safety of the cell at the time of overcharge with fluorine atom substituted aromatic compounds, It is required to carry out an addition to 3weight % or more, and in that case, even if it uses fluorine atom substitution aromatic combination, degradation of the battery characteristic under an elevated temperature becomes large.

[0010]As a method of improving the high temperature conservation characteristic of a cell, vinylene carbonate (JP,3066126,B), alkenyl ethylene carbonate (JP,2001-57232,A), and sultones (JP,H10-50342,A), Adding aromatic-sulfonic-acid ester species (JP,2002-158035,A) to an electrolysis solution is reported. It is possible to improve the high temperature conservation characteristic of a overcharge inhibitor by applying these methods to the electrolysis solution which added the overcharge inhibitor further. However, according to this invention person's examination, even if it used these additive agents for the cell which uses biphenyl as a overcharge inhibitor, there was almost no improving action of a high temperature conservation characteristic.

[0011]

[Patent documents 1] JP,H11-162512,A[0012]

[Problem to be solved by the invention]As stated above, the nonaqueous electrolyte which was excellent in the overcharge prevention characteristic and was excellent in the high temperature conservation characteristic, and a lithium secondary battery have not been obtained yet. Then, the overcharge preventive effect of this invention is high, and aims it at offer of nonaqueous electrolyte excellent in the high

temperature conservation characteristic. This invention is aimed at offer of the rechargeable battery which improved the safety at the time of overcharge including such nonaqueous electrolyte.

[0013]

[Means for solving problem]Namely, the aromatic hydrocarbon compound in which this invention consists only of a fluorine atom substituted aromatic compound, a carbon atom, and a hydrogen atom, It is an electrolysis solution which consists of other nonaqueous solvents and lithium content electrolytes, and the nonaqueous electrolyte which contains a fluorine atom substituted aromatic compound in an electrolysis solution, and contains 0.1 to 20 weight % and an aromatic hydrocarbon compound 0.1 to 3weight % in the electrolysis solution is provided.

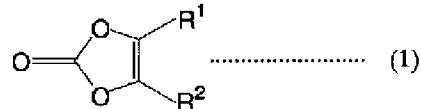
[0014]Said nonaqueous electrolyte which is at least one sort of compounds chosen from the group which the aforementioned fluorine atom substituted aromatic compound becomes from fluorine atom substitution naphthalene, fluorine atom substitution fluorenes, and fluorine atom substitution biphenyls is a desirable mode of this invention.

[0015]Said nonaqueous electrolyte which is at least one sort of compounds chosen from the group which the aforementioned aromatic hydrocarbon compound becomes from an alkyl group or cycloalkyl group substituted benzene, and biphenyls is a desirable mode of this invention.

[0016]The vinylene carbonate the aforementioned electrolysis solution is further indicated to be with a following general formula (1) as for this invention. The alkenyl ethylene carbonate shown with a following general formula (2), and the sultones which have an unsaturated hydrocarbon group shown with a following general formula (3). The nonaqueous electrolyte which contains at least one sort of compounds chosen from the sulfonic ester which has an aryl group expressed with a following general formula (4), the sultones which have a saturated hydrocarbon group, and the group which consists of sulfonic acidimide 0.01 to 10weight % in an electrolysis solution is provided. When these are used together with the mixture of a fluorine atom substituted aromatic compound and the aromatic hydrocarbon compound which consists only of a carbon atom and a hydrogen atom, a high temperature conservation characteristic can be improved substantially.

[0017]

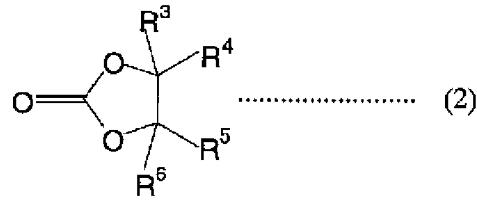
[Chemical formula 5]



In [type (1), R¹ and R² may be mutually the same, may differ from each other, and express the alkyl group in which the hydrogen atom, the halogen atom, or the carbon number may contain the halogen atom of 1-12.]

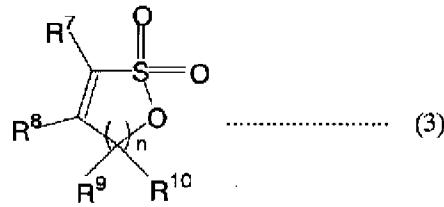
[0018]

[Chemical formula 6]



In [type (2), R³ - R⁶, It may be mutually the same and may differ, and a hydrogen atom, a halogen atom, the

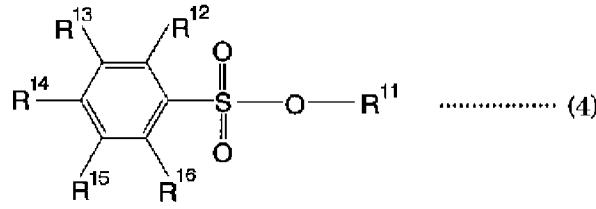
hydrocarbon group in which the carbon number may contain the halogen atom of 1-12, or a carbon number is an alkenyl group of 2-12, among those the carbon number of at least one is 2 - 12 alkenyl group.]
 [0019]
 [Chemical formula 7]



In [type (3), it is the alkyl group in which $R^7 - R^{10}$ may be mutually the same, it may differ, and the hydrogen atom, the halogen atom, or the carbon number may contain the halogen atom of 1-12, and n is an integer of 0 to 3.]

[0020]

[Chemical formula 8]



In [type (4), $R^{11} - R^{16}$, It may be mutually the same, may differ and A hydrogen atom, lithium atoms, It is the atom or basis chosen from the group which consists of a halogen atom, a sulfonic ester group, a carboxylate group, a sulfonic acid lithium base, and an alkyl group that may contain the halogen atom of the carbon numbers 1-12.]

[0021]Furthermore, this invention is a rechargeable battery containing an anode, a cathode, and an electrolysis solution, and provides the lithium secondary battery which is the nonaqueous electrolyte which the electrolysis solution described above.

[0022]This invention provides the aforementioned lithium secondary battery provided with the electric current breaker style which intercepts charge, if the gas pressure inside a cell becomes beyond a specified value.

[0023]This invention provides the aforementioned lithium secondary battery provided with the electric current breaker style which intercepts charge, if the temperature of a cell becomes beyond a specified value.

[0024]

[Mode for carrying out the invention]Next, the composition is concretely explained about the nonaqueous electrolyte concerning this invention, and the lithium secondary battery using the nonaqueous electrolyte. The aromatic hydrocarbon compound in which the nonaqueous electrolyte of this invention consists only of a fluorine atom substituted aromatic compound, a carbon atom, and a hydrogen atom, It is an electrolysis solution which consists of other nonaqueous solvents and lithium content electrolytes, and is nonaqueous electrolyte which contains a fluorine atom substituted aromatic compound in an electrolysis solution, and contains 0.1 to 20 weight %, and an aromatic hydrocarbon compound 0.1 to 3weight % in the electrolysis solution. Such nonaqueous electrolyte shows the outstanding overcharge preventive effect, and it can control the fall of a high temperature conservation characteristic as much as possible.

[0025]The fluorine atom substituted aromatic compound which is one ingredient of the nonaqueous electrolyte concerning fluorine atom substituted aromatic compound this invention is a substance which functions as a overcharge inhibitor, and some or all of a hydrogen atom that was combined with the aromatic ring is the compound replaced with the fluorine atom. The compound which has an aromatic ring here shows the ring compound with substantially stable delocalization of a pi electron.

[0026]As an example of such a compound, fluorine atom substituted benzene and fluorine atom substitution naphthalene. Fluorine atom ** decalins, fluorine atom substitution fluorenes, and fluorine atom substitution biphenyls. Fluorine atom substitution diphenylmethanes, fluorine atom substitution anthracene, Fluorine atom substitution terphenyl, fluorine atom substituted phenyl ether, fluorine atom substituted thiophenes, fluorine atom substitution francs, fluorine atom substitution pyrrole, fluorine atom substituted indole, fluorine atom substitution pyridines, etc. can be mentioned. Since [that a overcharge preventive effect has high fluorine atom substitution naphthalene, fluorine atom substitution fluorenes and fluorine atom substitution biphenyls in these and] degradation of a battery characteristic is small in comparison also under high temperature service, it is desirable, and fluorine atom substitution biphenyls are especially more preferred. These compounds may be used independently and may be used combining two or more kinds.

[0027]Next, the example of fluorine atom substitution naphthalene is given.

Fluorine atom substitution naphthalene : (1) 1-fluoronaphthalene, 2-fluoronaphthalene, 3-fluoronaphthalene, 1,2-difluoronaphthalene, 1,3-difluoronaphthalene, 1,4-difluoronaphthalene, 1,5-difluoronaphthalene, 1,6-difluoronaphthalene, 1,7-difluoronaphthalene, 1,8-difluoronaphthalene, 2,3-difluoronaphthalene, 2,6-difluoronaphthalene, 2,7-difluoronaphthalene, 1,3,5-trifluoronaphthalene, 1,3,7-trifluoronaphthalene, 1,3,5,7-tetrafluoro naphthalene, pentafluoro naphthalene, hexafluoro naphthalene, heptafluoro naphthalene, perfluoro naphthalene [0028](2) An alkyl group. And fluorine atom substitution naphthalene :. 1-fluoro-3-methylnaphthalene. (3) alkyloxy group and fluorine atom substitution naphthalene: -- 1-fluoro-3-methoxy naphthalene (4) chlorine atom and fluorine atom substitution naphthalene: -- a 1-fluoro-3-chloronaphthalene -- in the fluorine atom substitution naphthalene of these, As for the number of fluorine atom substitution per [the] molecule, 2-4 pieces are desirable. If the number of fluorine atom substitution is within the limits of the above, the outstanding overcharge preventive effect will be produced, and degradation of the battery characteristic under high temperature preservation becomes small.

[0029]Next, the example of fluorine atom substitution fluorenes is given.

Fluorine atom substitution fluorenes : (1) 1-fluorofluorene, 2-fluorofluorene, 3-fluorofluorene, 4-fluorofluorene, 9-fluorofluorene, A 1,2-difluorofluorene, a 1,3-difluorofluorene, a 1,4-difluorofluorene, A 1,5-difluorofluorene, a 1,6-difluorofluorene, a 1,7-difluorofluorene, An 1,8-difluorofluorene, a 2,3-difluorofluorene, a 2,6-difluorofluorene, A 2,7-difluorofluorene, a 2,8-difluorofluorene, a 3,4-difluorofluorene, A 3,5-difluorofluorene, a 3,6-difluorofluorene, a 4,5-difluorofluorene, A 9,9-difluorofluorene, a 1,3,5-trifluorofluorene, a 2,3,7-trifluorofluorene, a 1,3,5,7-tetrafluoro fluorene, a pentafluoro fluorene, a hexafluoro fluorene, a heptafluoro fluorene, a perfluoro fluorene [0030](2) An alkyl group. and fluorine atom substitution fluorenes: -- 1-fluoro-3-methylfluorene (3) alkyloxy group and fluorine atom substitution fluorenes: -- 1-fluoro-3-methoxy fluorene (4) chlorine atom and fluorine atom substitution fluorenes: -- a 1-fluoro-3-chlorofluorene

[0031]As for the number of fluorine atom substitution per [the] molecule, in these fluorine atom substitution fluorenes, 2-4 pieces are desirable. If the number of fluorine atom substitution is in this range, the outstanding overcharge preventive effect will be acquired and degradation of the battery characteristic under

high temperature preservation will become small.

[0032]Next, the example of fluorine atom substitution biphenyls is given.

Fluorine atom substitution biphenyls : (1) 2-fluorobiphenyl, 3-fluorobiphenyl, 4-fluorobiphenyl, 2,3-difluorobiphenyl, 2,4-difluorobiphenyl, 2,5-difluorobiphenyl, 2,6-difluorobiphenyl, 2,2'-difluorobiphenyl, 2,3'-difluorobiphenyl, 2,4'-difluorobiphenyl, 2,5'-difluorobiphenyl, 2,6'-difluorobiphenyl, 3,3'-difluorobiphenyl, 3,4'-difluorobiphenyl, 3,5'-difluorobiphenyl, 3,6'-difluorobiphenyl, 4,4'-difluorobiphenyl, trifluorobiphenyl, tetrafluorobiphenyl, pentafluoro biphenyl, hexafluoro biphenyl, heptafluoro biphenyl, octafluoro biphenyl, nonafluoro biphenyl, perfluoro biphenyl [0033](2) An alkyl group and fluorine atom substitution biphenyl 2-fluoro-4-methylbiphenyl, A 4-fluoro-2-methylbiphenyl and 2-fluoro-2'-methylbiphenyl (3) alkyloxy group and fluorine atom substitution biphenyl 2-fluoro-4-methoxy biphenyl, A 4-fluoro-2-methoxy biphenyl and 2-fluoro-2'-methoxy biphenyl (4) chlorine atom and fluorine atom substitution biphenyl 2-fluoro-4-chlorobiphenyl

[0034]In such fluorine atom substitution biphenyls, as for the number of fluorine atom substitution per [the] molecule, 1-3 pieces are preferred, one piece or two pieces are more preferred, and its one piece is still more preferred. If the number of fluorine atom substitution is in the aforementioned range, the outstanding overcharge preventive effect will be acquired.

[0035]The fluorine atom replacement positions have two positions or four desirable positions, and its further 2 positions are [case of fluorine atom mono- substitution biphenyls] the most desirable. If two positions are replaced, not only according to the electronic suction effect of a fluorine atom but according to a steric effect, the electrolysis voltage of biphenyl can be controlled, and degradation of the battery characteristic under high temperature preservation can be controlled as much as possible, and a overcharge preventive effect can be heightened.

[0036]The fluorine atom replacement positions have two positions of two rings, or four desirable positions, and further 4 positions and its 4' position are [case of ***** substitution biphenyls] the most desirable. If the fluorine atom has combined with the aforementioned replacement positions, the electrolysis voltage of biphenyl can be controlled moderately, degradation of the battery characteristic under high temperature preservation can be controlled, and a overcharge preventive effect can be heightened.

[0037]Also in the above mentioned fluorine atom substitution biphenyls, 2-fluorobiphenyl, 4-fluorobiphenyl, and 4,4'-difluorobiphenyl are preferred, and 2-fluorobiphenyl is especially preferred.

[0038]In the nonaqueous electrolyte concerning aromatic hydrocarbon compound this invention, the aromatic hydrocarbon compound which consists only of a carbon atom and a hydrogen atom as one of constituents is added. By it, the effect which heightens further the overcharge preventive effect of a fluorine atom substituted aromatic compound can be acquired. As such an aromatic hydrocarbon compound, benzens, biphenyls, terphenyl, and naphthalene can be mentioned, and they may use one kind and may use it combining two or more kinds.

[0039]Next, the example of these aromatic hydrocarbon compounds is given.

Benzens : (1) Benzene, toluene, xylene, a cumene, cyclohexylbenzene, Tetralin (2) biphenyls : Biphenyl, 2-methylbiphenyl, 3-methylbiphenyl, 4-methylbiphenyl, 2-ethylbiphenyl, 2,2'-dimethylbiphenyl (3) terphenyl:

Alt.terphenyl, meta-terphenyl, Para Taaffe Nils, methyl terphenyl (4) naphthalene:naphthalene, 1-methylnaphthalene, 2-methylnaphthalene [0040]Also in these aromatic hydrocarbon compounds, an alkyl group or cycloalkyl group substituted benzene, and biphenyls are preferred, cyclohexylbenzene and biphenyl are still more preferred, and biphenyl is the most preferred. The overcharge preventive effect of a

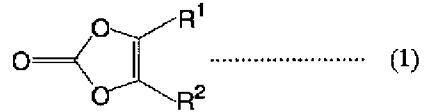
fluorine atom substituted aromatic compound can be heightened making the fall of the battery characteristic at the time of high temperature preservation into the minimum, when adding a little these compounds.

[0041] In the nonaqueous electrolyte concerning other compound this inventions. To two described ingredients, previously In addition, the vinylene carbonate further shown by a general formula (1). The alkenyl ethylene carbonate shown by a general formula (2), and the sultones which have an unsaturated hydrocarbon group shown by a general formula (3). It is desirable to add at least one sort of compounds chosen from the sulfonic ester which has an aryl group expressed with a general formula (4), the sultones which have a saturated hydrocarbon group, and the group which consists of sulfonic acidimide.

[0042] In the case of two ingredients which the overcharge inhibitor showed previously, the fall of the battery characteristic at the time of the high temperature preservation which happens by adding a overcharge inhibitor can be substantially controlled by adding an above-mentioned compound. The compound described below can be illustrated as an above-mentioned compound. They may be used independently and may be used combining two or more kinds.

(1) The aryl group expressed with the sultones (4) general formula (4) which has an unsaturated hydrocarbon group shown by the alkenyl ethylene carbonate (3) general formula (3) shown by the vinylene carbonate (2) general formula (2) shown by a general formula (1). Sultones (6) sulfonic-acidimide which has a sulfonic ester (5) saturated hydrocarbon group which it has [0043]Vinylene carbonate is expressed with the general formula (1) shown below.

[Chemical formula 9]

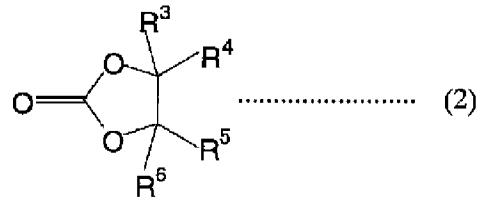


[0044] In a formula (1), R¹ and R² may be mutually the same, may differ from each other, and express the alkyl group in which the hydrogen atom, the halogen atom, or the carbon number may contain the halogen atom of 1-12. As a halogen atom, a fluorine atom or a chlorine atom is preferred, and a fluorine atom is still more preferred.

[0045] As an example of vinylene carbonate expressed with a formula (1), vinylene carbonate, Fluoro vinylene carbonate, methyl vinylene carbonate, fluoromethyl vinylene carbonate, Ethyl vinylene carbonate, propyl vinylene carbonate, butyl vinylene carbonate, dimethyl vinylene carbonate, diethyl vinylene carbonate, dipropyl vinylene carbonate, etc. can be mentioned. Vinylene carbonate is the most desirable among these compounds.

[0046] Alkenyl ethylene carbonate is expressed with the general formula (2) shown below.

[Chemical formula 10]



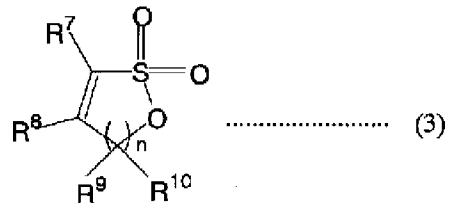
[0047] In a formula (2), R³ - R⁶, The hydrocarbon group in which it may be mutually the same, and may differ and the hydrogen atom, the halogen atom, and the carbon number may contain the halogen atom of 1-12,

Or a carbon number is an alkenyl group of 2-12, and at least one carbon number in R³ - R⁶ is 2 - 12 alkenyl group. As an example of an alkenyl group, a vinyl group, a propenyl group, an allyl group, a butenyl group, etc. can be mentioned.

[0048]As an example of alkenyl ethylene carbonate expressed with a formula (2), Vinyl ethylene carbonate, propenyl ethylene carbonate, 4,4-divinyl ethylene carbonate, 4,5-divinyl ethylene carbonate, 4-methyl-4-vinyl ethylene carbonate, 4-fluoro-4-vinyl ethylene carbonate, 4-fluoro-5-vinyl ethylene carbonate, 4-methyl-5-vinyl ethylene carbonate, 4-ethyl-4-vinyl ethylene carbonate, etc. can be mentioned. Vinyl ethylene carbonate and divinyl ethylene carbonate are the most desirable among these compounds.

[0049]The sultones which have an unsaturated hydrocarbon group are expressed with the general formula (3) shown below.

[Chemical formula 11]

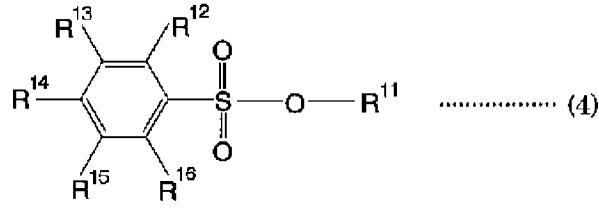


[0050]In a formula (3), it is the alkyl group in which R⁷ - R¹⁰ may be mutually the same, it may differ, and the hydrogen atom, the halogen atom, or the carbon number may contain the halogen atom of 1-12, and n is an integer of 0 to 3.

[0051]As an example of the sultones which have an unsaturated hydrocarbon group expressed with a formula (3), An ethylene sultone, a 1,3-propene sultone, a 1,4-butene sultone, A 1,5-pentene sultone, a 1-methyl-1,3-propene sultone, A 1-fluoro-1,3-propene sultone, a 2-methyl-1,3-propene sultone, a 3-methyl-1,3-propene sultone, a 1-trifluoromethyl 1,3-propene sultone, etc. can be mentioned. Also among these compounds, a 1,3-propene sultone and a 1,4-butene sultone are the most desirable.

[0052]As sulfonic ester which has an aryl group, the thing of the general formula (4) shown below is illustrated.

[Chemical formula 12]



[0053]In a formula (4), R¹¹ - R¹⁶, It may be mutually the same, may differ and A hydrogen atom, lithium atoms, It is the atom or basis chosen from the group which consists of a halogen atom, a sulfonic ester group, a carboxylate group, a sulfonic acid lithium base, and an alkyl group that may contain the halogen atom of the carbon numbers 1-12.

[0054]As an example of the sulfonic ester which has an aryl group expressed with a formula (4), Ethyl benzenesulfonate, BENZENJI (sulfonic acid methyl), BENZENJI (sulfonic acid ethyl), BENZENJI (sulfonic acid propyl), benzene (sulfonic acid methyl) (sulfonic acid ethyl), BENZENJI (sulfonic acid allyl), BENZENJI (sulfonic acid vinyl), BENZENJI (sulfonic acid ethynyl), a benzene bird (sulfonic acid methyl), A

sulfobenzonic acid anhydride, sulfobenzonic acid dimethyl, methyl toluenesulfonic acid, Torr ENJI (sulfonic acid ethyl), a toluene bird (sulfonic acid propyl), Trifluoromethyl methyl benzenesulfonate, trifluoromethyl BENZENJI (sulfonic acid methyl), A trifluoromethyl benzene bird (sulfonic acid ethyl), naphthalene sulfonic acid lithium salt, Benzenesulfonic acid lithium salt, trifluoromethyl benzenesulfonic acid lithium salt, A benzenedisulfonic acid dilithium salt, a trifluoromethyl benzenedisulfonic acid dilithium salt, benzene trisulfonic acid bird lithium salt, a sulfobenzonic acid dilithium salt, toluenesulfonic acid lithium salt, A toluene disulfon acid dilithium salt etc. can be mentioned. Also in these compounds, BENZENJI (sulfonic ester) is preferred and BENZENJI (sulfonic ester) of meta-position substitution is especially preferred.

[0055]As sultones which have a saturated hydrocarbon group, 1, 3 **PURO bread sultone, 1, 4 **BUTAN sultone, a 1,5-pentanesultone, a 1,6-hexane sultone, The 1-methyl 1, 3 **PURO bread sultone, 2 **MECHIRU 1, 3 **PURO bread sultone, 3 **MECHIRU 1, 3 **PURO bread sultone, 1 *****- 1, 4 **BUTAN sultone, 2 *****- 1, 4 **BUTAN sultone, 3 *****- 1, 4 **BUTAN sultone, 4 *****- 1, 4 **BUTAN sultone, etc. can be illustrated. 1, 3 **PURO bread sultone, and 1 and 4 **BUTAN sultone are [among these] desirable.

[0056]As sulfonic acidimide, N*****-** (methanesulfonic acid) imide, N,N-dimethyl- methanesulfon acid imide, tris(trifluoromethanesulfonic acid)imide, N*****-** (trifluoromethanesulfonic acid) imide, JI (trifluoromethanesulfonic acid) imide lithium salt, N,N-dimethyl- trifluoro methanesulfon acid imide, N*****-** (trifluoromethanesulfonic acid) imide, N,N-diethyl- trifluoro methanesulfon acid imide, N*****-** (pentafluoro ethane sulfonic acid) imide, JI (pentafluoro ethane sulfonic acid) imide lithium salt, N,N-dimethyl- pentafluoro imidethane sulfonic acid, N*****-** (perfluoro propanesulfonic acid) imide, N,N-dimethyl- perfluoro imidopropanesulfonate, N*****-** (perfluoro butanesulfonic acid) imide, and N,N-dimethyl- perfluoro imidobutanesulfonate can be illustrated.

[0057]Also in these compounds, JI (trifluoromethanesulfonic acid) imide. JI (pentafluoro ethane sulfonic acid) imide is preferred, and since especially JI (trifluoromethanesulfonic acid) imide lithium salt and JI (pentafluoro sulfonic acid) imide lithium salt act also as an electrolyte and raise the ion conductivity of an electrolysis solution, they are desirable.

[0058]The vinylene carbonate expressed with a general formula (1) among the above mentioned compounds and the sultones which have an unsaturated hydrocarbon group expressed with a general formula (3) are desirable. Specifically, vinylene carbonate and a 1,3-propene sultone are preferred.

[0059]If the vinylene carbonate expressed with a general formula (1) and the sultones which have an unsaturated hydrocarbon group expressed with a general formula (3) are added simultaneously, It is desirable in order to multiply and add the effect of high-temperature-preservation nature, and the combination of vinylene carbonate and a 1,3-propene sultone can be mentioned as the example.

[0060]the aromatic hydrocarbon compound in which the nonaqueous electrolyte concerning other nonaqueous solvent this inventions comprises a nonaqueous solvent and an electrolyte fundamentally, and the nonaqueous solvent consists only of said fluorine atom substituted aromatic compound carried out, and a carbon atom and a hydrogen atom -- in addition, the nonaqueous solvent by which normal use is carried out is used. Here, "the nonaqueous solvent by which normal use is carried out" is called "other nonaqueous solvents", and is explained concretely below.

[0061]As a nonaqueous solvent of usable others, an annular aprotic solvent and/or chain aprotic solvent can be mentioned. Cyclic ether like cyclic carbonate like ethylene carbonate, cyclic ester like gamma-

butyrolactone, an annular sulfone like sulfolane, and dioxolane as an annular aprotic solvent can be illustrated among them. As a chain aprotic solvent, chain carbonate like dimethyl carbonate, chain carboxylate like methyl propionate, and chain ether like dimethoxyethane can be illustrated.

[0062]When especially the improvement in the load characteristic of a cell or the low-temperature characteristic is meant, it is desirable to mix and use an annular aprotic solvent and a chain aprotic solvent. When thinking the electrochemical stability of an electrolysis solution as important, it is desirable to choose cyclic carbonate as an annular aprotic solvent, to choose chain carbonate as a chain aprotic solvent, and to carry out mixed use.

[0063]As an example of cyclic carbonate, ethylene carbonate, propylene carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-pentylene carbonate, and 2,3-pentylene carbonate can be mentioned. High ethylene carbonate and propylene carbonate of a dielectric constant are preferred. Ethylene carbonate is preferred especially when using black lead for negative electrode active material. These cyclic carbonate may carry out mixed use of the two or more kinds.

[0064]As an example of chain carbonate, dimethyl carbonate, methylethyl carbonate, Diethyl carbonate, methylpropyl carbonate, methyliso propyl carbonate, dipropyl carbonate, methylbutyl carbonate, dibutyl carbonate, ethylpropyl carbonate, and methyl trifluoroethyl carbonate can be mentioned. Dimethyl carbonate with low viscosity, methylethyl carbonate, and diethyl carbonate can be used conveniently. These chain carbonate may carry out mixed use of the two or more kinds.

[0065]expressing the mixing ratio (cyclic carbonate: chain carbonate) of cyclic carbonate and chain carbonate with a weight ratio -- desirable -- 1:99-99:1 -- more -- desirable -- 5:95-70:30 -- it is 10:90-60:40 still more preferably. Since a viscosity rise of an electrolysis solution can be controlled as it is within the limits of such the mixing ratio, and an electrolytic degree of disassociation can be raised, the conductivity of the electrolysis solution in connection with the charging and discharging characteristic of a cell can be raised.

[0066]On the other hand, it is desirable to adjust the mixing ratio of a chain aprotic solvent to 20 or less weight % to the other whole nonaqueous solvents as other nonaqueous solvents independently, using an annular aprotic solvent, in making the flash point of a solvent high from a viewpoint of the improvement in fire safety of a cell.

[0067]It is desirable to use especially as an annular aprotic solvent in this case combining one sort or these which are chosen from ethylene carbonate, propylene carbonate, sulfolane, gamma-butyrolactone, and N-methyl OKISAZO linon. As a combination of a concrete solvent, ethylene carbonate, sulfolane and ethylene carbonate, propylene carbonate and ethylene carbonate, gamma-butyrolactone and ethylene carbonate, propylene carbonate, and gamma-butyrolactone can be mentioned.

[0068]When using a chain aprotic solvent at 20 or less weight % of a rate to the other whole nonaqueous solvents, chain carbonate, chain carboxylate, and chain phosphoric ester can be used as a chain aprotic solvent. Especially Dimethyl carbonate, diethyl carbonate, dipropyl carbonate, Chain carbonate, such as dibutyl carbonate, diheptyl carbonate, dioctyl carbonate, methylethyl carbonate, methylpropyl carbonate, methylbutyl carbonate, methylheptyl carbonate, and methyloctyl carbonate, is desirable. The mixing ratio (cyclic carbonate: chain carbonate) of cyclic carbonate and chain carbonate is expressed with a weight ratio, and 80:20 to 99.5:0.5 is desirable, and also 90:10-99:1 are desirable.

[0069]The solvent except said may be included in other nonaqueous solvents within limits which do not

deviate from the purpose of this invention. As such a solvent, specifically Amide, such as dimethylformamide. Chain Cava mates, such as a methyl-N,N-dimethyl carver mate. Annular urea, such as cyclic amide, such as N-methyl pyrrolidone, and N,N-dimethylimidazolidinone. Way acid trimethyl ** way acid triethyl, way acid tributyl, way acid trioctyl, The ester of boric acid, such as a way acid bird (trimethylsilyl), trimethyl phosphate, Phosphoric acid triethyl, chain phosphoric ester like tris phosphite (trimethylsilyl), and ethyleneglycol dimethyl ether, An ethylene glycol derivative like diethylene glycol dimethyl ether and polyethylene-glycols wood ether, etc. can be illustrated.

[0070]As an electrolyte which contains usable lithium in the nonaqueous electrolyte of lithium content electrolyte this invention, if used as an electrolyte for nonaqueous electrolyte, all can usually be used, without being restricted especially.

[0071]As an electrolytic example, LiPF₆, LiBF₄, LiClO₄, LiAsF₆, Li₂SiF₆, Lithium salt, such as LiOSO₂C_kF_(2k+1) (integer of k= 1-8) and LiPF_n{C_kF_(2k+1)}_(6-n) (the integer of n= 1-5, the integer of k= 1-8), is mentioned.

[0072]The lithium salt shown by the following general formula can also be used. Namely, LiC(SO₂R¹⁷)(SO₂R¹⁸)(SO₂R¹⁹), LiN(SO₂OR²⁰)(SO₂OR²¹), LiN(SO₂R²²)(SO₂OR²³), LiN(SO₂R²⁴)(SO₂R²⁵). Here, R¹⁷ - R²⁵ may be mutually the same, may differ from each other, and are a perfluoroalkyl group of the carbon numbers 1-8. LiPF₆, LiBF₄, and LiN(SO₂R²⁴)(SO₂R²⁵) are [among these] preferred especially.

[0073]Although some compounds illustrated here overlap with the above mentioned sulfonic acidimide selectively, Since those compounds have the effect which controls degradation of the battery characteristic under the high temperature service of nonaqueous electrolyte at the same time they act as an electrolyte, it is desirable to use it for which purpose and to use it as a lithium content electrolyte.

[0074]These lithium salt may be used alone, and may mix and use two or more kinds. As a combination which mixes and uses two or more kinds, LiPF₆, LiBF₄ and LiPF₆, and LiN(SO₂R²⁴)(SO₂R²⁵), LiBF₄, LiN(SO₂R²⁴)(SO₂R²⁵), and LiPF₆, LiBF₄ and LiN(SO₂R²⁴)(SO₂R²⁵) are illustrated.

[0075]un--- Water Electrolysis The nonaqueous electrolyte concerning liquid this invention contains at least the fluorine atom substituted aromatic compound, the aromatic hydrocarbon compound which consists only of a carbon atom and a hydrogen atom, the nonaqueous solvent containing other nonaqueous solvents, and the lithium content electrolyte as the constituent.

[0076]3 to 20 weight % and further 3 to 10 weight % are still more preferably desirable [the content of a fluorine atom substituted aromatic compound] 0.5 to 20weight % preferably 0.1 to 20weight % to the whole electrolysis solution. A high overcharge preventive effect is acquired as it is this within the limits, and since the fall of a high temperature conservation characteristic is suppressed to the minimum and there is almost no fall of the lithium ion conductivity of an electrolysis solution, the load characteristic of a cell can be kept good.

[0077]0.1 to 1 weight % is more preferably desirable [the content of the aromatic hydrocarbon compound which consists only of a carbon atom and a hydrogen atom] 0.1 to 2weight % preferably 0.1 to 3weight % to the whole electrolysis solution. The overcharge preventive effect which was excellent according to the

synergistic effect with a fluorine atom substituted aromatic compound in it being this within the limits is acquired, and the fall of the battery characteristic at the time of high temperature preservation is also controlled to the minimum.

[0078]As for a lithium content electrolyte, it is desirable to contain 0.1-3 mol/l. in nonaqueous electrolyte by the concentration of 0.5-2 mol/l. more preferably. By it, electrical properties, such as a good load characteristic and the low-temperature characteristic, can be acquired.

[0079]the basic constitution which contains the nonaqueous solvent and electrolyte of said fluorine atom substituted aromatic compound carried out, the aromatic hydrocarbon compound which consists only of a carbon atom and a hydrogen atom, and others as one mode of the nonaqueous electrolyte concerning this invention -- in addition, it is changeable to the composition which added the further above-mentioned "other compounds." 0.1 to 3 weight % is still more preferably desirable [the content] 0.05 to 5weight % more preferably 0.01 to 10weight % preferably to the whole electrolysis solution. If an addition is within the limits of this, the fall of the battery characteristic at the time of the high temperature preservation which happens when the above mentioned overcharge inhibitor is added can be controlled substantially.

[0080]It is not only suitable as nonaqueous electrolyte for lithium secondary batteries, but it can use the nonaqueous electrolyte concerning this invention of composition of having mentioned above as the nonaqueous electrolyte for primary batteries, the nonaqueous electrolyte for electrochemical capacitors, and nonaqueous electrolyte for an electric double layer capacitor or aluminium electrolytic condensers.

[0081]2 s following -- The lithium secondary battery concerning cell this invention comprises fundamentally an anode, a cathode, a separator that separates them mutually, and said nonaqueous electrolyte carried out.

[0082]As negative electrode active material which constitutes an anode, metal lithium, a lithium content alloy, Or the silicon in which alloying with lithium is possible, a silicon alloy, tin, A tin alloy, the tin oxide in which the dope and dedope of a lithium ion are possible, silicon oxide, Either the transition metal oxide in which the dope and dedope of a lithium ion are possible, the transition metal nitrogen compound in which the dope and dedope of a lithium ion are possible the carbon materials in which the dope and dedope of a lithium ion are possible or these mixtures can be used.

[0083]As a carbon material, carbon black, activated carbon, an artificial graphite, natural graphite, amorphous carbon material, etc. can be mentioned. The form may be any, such as fibrous, a globular shape, the shape of a potato, and the shape of flakes. As an amorphous carbon material, hard carbon, corks, the meso carbon micro beads (MCMB) calcinated below 1500 **, a mesophase pitch carbon fiber (MCF), etc. can specifically be illustrated. As a graphite material, natural graphite, graphitization corks, the graphitization MCMB, graphitization MCF, etc. can use the thing containing boron, the thing further covered with metal, such as gold, platinum, silver, copper, Sn, and Si, or the thing covered with amorphous carbon. One kind may be used for these carbon materials, and they may carry out mixed use, combining two or more kinds suitably. Carbon black, amorphous whisker carbon, etc. may be used as an electric conduction auxiliary agent, adding.

[0084]Especially as a carbon material, a carbon material of 0.340 nm or less has a preferred spacing (d002) of the field (002) measured with the X-ray diffraction method, and the high crystallinity carbon material which has character with the true density near black lead or it which is more than 1.70 g/cm³ is desirable. If such a carbon material is used, energy density of a cell can be made high.

[0085]As positive active material which constitutes a cathode, FeS_2 , MoS_2 , Transition metal sulfide or transition metal oxides, such as TiS_2 , MnO_2 , and V_2O_5 , LiCoO_2 , LiMnO_2 , LiMn_2O_4 , LiNiO_2 , $\text{LiNi}_{x}\text{Co}_{(1-x)}\text{O}_2$, The multiple oxide of lithium, such as $\text{LiNi}_x\text{Co}_y\text{Mn}_{(1-x-y)}\text{O}_2$, and a transition metal, Carbon materials, such as conductive polymers, such as poly aniline, a polythiophene, polypyrrole, polyacetylene, poly acene, and a dimercapto thiadiazole poly aniline complex, fluorinated carbon, and activated carbon, etc. can be mentioned.

[0086]Also in these, since the increase in the cell voltage at the time of overcharge is large, especially the multiple oxide of lithium and a transition metal is [that it is easy to electrolyze a overcharge inhibitor] preferred. Positive active material may use one kind and may carry out mixed use of the two or more kinds. Since conductivity of positive active material is not usually enough, it constitutes a cathode using both electric conduction auxiliary agents. As such an electric conduction auxiliary agent, carbon materials, such as carbon black, amorphous whisker carbon, and graphite, can be illustrated.

[0087]The separator should just be a film which can insulate a cathode and an anode electrically and can penetrate a lithium ion, and porous membrane and a polymer electrolyte are used. As porous membrane, a fine porosity high polymer film is used suitably, and polyolefine, polyimide, polyvinylidene fluoride, polyester, etc. are illustrated as construction material. In particular, a porous polyolefin film is preferred and the multilayer film of a porous polyethylene film, a porous polypropylene film or a porous polyethylene film, and a polypropylene film can specifically be illustrated. On these porosity polyolefin film, it may coat with other resin excellent in thermal stability.

[0088]As a polymer electrolyte, the polymeric material which dissolved lithium salt, the polymeric material which swelled with the electrolysis solution, etc. are mentioned. The nonaqueous electrolyte of this invention may be used in order to swell a polymeric material and to obtain a polymer electrolyte.

[0089]The lithium secondary battery of such composition can be formed in cylindrical, a coin type, a square shape, a film mold, and other arbitrary form. However, the basic structure of a cell is not based on form, but is almost the same and can perform a change of design according to the purpose.

[0090]In order to demonstrate the overcharge preventive effect which nonaqueous electrolyte has in the lithium secondary battery concerning this invention, When the temperature of the electric current breaker style which will intercept charge if the gas pressure inside a cell becomes beyond a specified value, and/or a cell becomes beyond a specified value, it is preferred to have the electric current breaker style which intercepts charge.

[0091]If a cell is generally overcharged, an electrolysis solution will be electrolyzed and gas and heat will be generated. The above mentioned electric current breaker style is a mechanism in which this gas and/or heat are detected, charge of a cell is intercepted, and a cell prevents overcharging. Since gas and heat occur at the time of this electrolysis other than the function which will be electrolyzed if the voltage of a cell becomes high beyond constant value, and cannot follow charge of a cell any more, the nonaqueous electrolyte concerning this invention can operate an electric current breaker style early. Therefore, the safety at the time of overcharge of a cell can be improved further.

[0092]As an electric current breaker style which will intercept charge if the gas pressure inside a cell becomes beyond a specified value, The mechanism in which it changes when the internal pressure of a cell rises, and a charging current point of contact goes out, The external circuit which detects the internal

pressure of a cell by a sensor and suspends charge, the external circuit which detects modification of the cell by the internal pressure of a cell by a sensor, and suspends charge, the mechanism in which change when the internal pressure of a cell rises, and a cathode and an anode are short-circuited, and a cell is made not to charge, etc. can be illustrated. Among this, the mechanism in which it changes when the internal pressure of a cell rises, and the point of contact of charging current goes out is a simple structure, and since the effect is high, it is preferred.

[0093]As an electric current breaker style which will intercept charge if the temperature of a cell becomes beyond a specified value, The separator which will carry out melting, will cause blinding and will prevent passage of ion if the temperature of the external circuit and cell which detect the rise in heat of a cell by a sensor, and suspend charge rises, The capsules which will diffuse the inactivation substance of a cell if the temperature of a cell rises. If the temperature of the mechanism and cell by which melting will be carried out and the point of contact of charging current will go out if the temperature of the element and cell by which electrical resistance will rise if the temperature of a cell rises rises rises, the electrode having contained the conducting material with which electrical resistance rises can be illustrated.

[0094]Next, although an example of the structure of cylindrical and a coin type cell is explained, the above mentioned thing can be used for the negative electrode active material, the positive active material, and the separator which constitute each cell in common.

[0095]With the cylindrical lithium secondary battery, where an electric insulating plate is laid in the upper and lower sides of winding and a winding body via the separator which poured in nonaqueous electrolyte for the anode which applied negative electrode active material to negative pole collectors, such as copper foil, and the cathode which applied positive active material to positive pole collectors, such as aluminium foil, it is stored by the battery can. And if the current point of contact which will change and go out if the internal pressure of a cell rises, and the temperature of a cell rise, it has structure which covered the battery can and closed the end of the battery can to it using the obturation object in which the element for which electrical resistance rises was attached.

[0096]In the coin type lithium secondary battery, [the separator, the disc-like cathode and if needed] of having poured in a disc-like anode and nonaqueous electrolyte, spacer boards, such as stainless steel or aluminum, are stored by the coin type cell can, after this order has laminated. The strain gage etc. which detect modification of the cell by the internal pressure of a cell may be attached.

[0097]

[Working example]Next, although this invention is explained more to details through an embodiment, this invention is not restricted at all by those embodiments.

[0098]1. As a production <preparation of nonaqueous electrolyte> nonaqueous solvent of a cell, ethylene carbonate (EC) and methylethyl carbonate (MEC) are mixed at a rate of EC:MEC=4:6 (weight ratio), Next, it dissolved in the nonaqueous solvent which described above LiPF₆ which is an electrolyte, and nonaqueous electrolyte was prepared so that electrolytic concentration might become [I.] in 1.0 mol /.

[0099]Next, specified quantity addition of various kinds of compounds indicated to Table 1 was carried out to this nonaqueous electrolyte, and 19 kinds of electrolysis solutions were prepared. In Table 1, the kind of additive agent was performed as follows abbreviated, and was described.

FBP: 2-fluorobiphenyl, BP:biphenyl, VC : Vinylene carbonate, PES: A 1,3-propene sultone, DPM:diphenylmethane, CHB : Cyclohexylbenzene, BD: Meta-benzenedisulfonic-acid dimethyl ester, TF: A

JI (trifluoromethanesulfonic acid) imidelithium PS:1,3-propane sultone and the numerical value in a parenthesis are values which showed the content in the electrolysis solution of each compound by weight %.

[Table 1]

電解液	フッ素原子置換 芳香族化合物	炭素と水素のみから なる芳香族化合物	その他の化合物
電解液 1	なし	なし	なし
電解液 2	F B P (3.0)	なし	なし
電解液 3	F B P (3.0)	B P (0.1)	なし
電解液 4	F B P (3.0)	B P (0.3)	なし
電解液 5	F B P (3.0)	B P (0.5)	なし
電解液 6	F B P (3.0)	B P (1.0)	なし
電解液 7	F B P (3.0)	C H B (1.0)	なし
電解液 8	F B P (3.0)	B P (0.5)	P E S (0.5)
電解液 9	F B P (3.0)	B P (0.5)	V C (1.0)
電解液 10	F B P (3.0)	B P (0.5)	P E S (0.5) V C (1.0)
電解液 11	F B P (3.0)	B P (0.5)	B D (0.5) V C (1.0)
電解液 12	F B P (3.0)	B P (0.5)	T F (2.0) V C (1.0)
電解液 13	F B P (3.0)	B P (0.5)	P S (1.0) V C (1.0)
電解液 14	F B P (3.0)	C H B (0.5)	P E S (0.5) V C (1.0)
電解液 15	F B P (3.0)	B P (1.0)	P E S (0.5) V C (1.0)
電解液 16	なし	B P (3.0)	なし
電解液 17	なし	B P (3.0)	P E S (0.5) V C (1.0)
電解液 18	なし	D P M (4.0)	P E S (1.0) V C (1.0)
電解液 19	なし	C H B (3.0)	P E S (1.0) V C (1.0)

[0100]<Production of anode> meso-carbon-micro-beads (Osaka Gas Co., Ltd. make MCMB10-28) 74 weight section, Natural graphite (Chuetsu Graphite Works LF18A) 20 weight section and polyvinylidene fluoride (PVDF) 6 weight section of the binding agent were mixed, N-methylpyrrolidinone of the solvent was distributed, and the negative electrode mixture slurry was prepared. Next, this negative electrode mixture slurry was applied to the 18-micrometer-thick negative pole collector made from band-like copper foil, and it dried.

[0101]<Production of cathode> LiCoO₂ (product [made from Honjo FMC Energy Systems] HLC-22) 82 weight section, Black lead 7 weight section of a conducting agent, acetylene black 3 weight section, and polyvinylidene fluoride 8 weight section of the binding agent were mixed, N-methyl pyrrolidone of the solvent was distributed, and LiCoO₂ mixture slurry was prepared. This LiCoO₂ mixture slurry was applied to 20-micrometer-thick aluminum foil, and it dried.

[0102]In the anode for <production of coin type cell> coin type cells, compression molding of the aforementioned anode was carried out, it pierced to discoid 14 mm in diameter, and the coin-like anode was obtained. The thickness of negative electrode mixture was 70 micrometers, and weight was 20-mg/14mmphi. In the cathode for coin type cells, compression molding of the aforementioned cathode was carried out, it pierced to discoid 13.5 mm in diameter, and the coin-like LiCoO₂ cathode was obtained.

LiCoO₂ -- the thickness of the mixture was 70 micrometers and weight was 42-mg/13.5mmphi. The anode 14 mm in diameter, the cathode 13.5 mm in diameter, and the separator that was able to be done from a fine porosity polypropylene film 16 mm in diameter at 25 micrometers in thickness were laminated in order of the anode, the separator, and the cathode in the battery can of 2032 sizes made from stainless steel. Then, 0.04 ml of the aforementioned nonaqueous electrolyte was poured into the separator, and the board (1.2 mm in thickness and 16 mm in diameter) and spring of further the product made from aluminum were stored. Finally, by closing a battery can lid via the gasket made from polypropylene, the airtightness in a cell was

held and a coin type cell 20 mm in diameter and 3.2 mm in height was produced.

[0103]Cut down the anode with a size of 21 mm x 21 mm and the cathode with a size of 20 mm x 20 mm with having done the <production of laminated battery> above of using the same electrode, and it was made to counter via the separator which was able to be done from the fine porosity polypropylene film with a 25 mm[in width] x length of 50 mm, and was considered as the electrode body. It accommodated so that both the leads of a cathode and an anode might be pulled out from releasing part of one of the two by the tubed bag which produced this electrode body with the aluminum laminate film (product made from Showa Lamination Industry), and thermal melting arrival carried out the side by which the lead was pulled out, and it closed. Next, inject 0.15 ml of electrolysis solutions into an electrode body, and they were made to impregnate, thermal melting arrival of the releasing part which remained was carried out after that, the electrode body was sealed in the bag, and the laminated battery was obtained.

[0104]2. The laminated battery of the evaluation <measurement of gas yield at time of valuation method 1:overcharge of overcharge preventive effect> above-mentioned of the battery characteristic was charged 4.1V, the charge and discharge of 4.2V to 3.0V were performed after 24-hour preservation at 45 **, and the capacity of the cell was checked. The capacity of the cell at this time was 10mAh. This cell was charged by 5-mA constant current for 5 hours, and the cell was made to overcharge. The capacity of the cell before overcharge and the capacity of the cell after overcharge were measured, and the generating gas volume at the time of overcharge was measured from the difference. The measurement result of the gas volume generated at the time of the kind of electrolysis solution used for measurement and overcharge was shown in Table 2.

[0105]The valuation method 2 of < overcharge preventive effect : the oxidation potential of the measurement > electrolysis solution of the oxidation current of an electrolysis solution, In the glove box, where an electrolysis solution is heated at 80 **, glassy carbon, the counter electrode, and the reference pole were used as metal lithium for the working pole, and in 3V-5V, cyclic voltammetry was performed in sec in 10mV /, and it measured. Since a cell will generate heat with the electrolysis heat of an electrolysis solution if having measured at 80 ** overcharges a cell, it is because the oxidation current of the electrolysis solution in an elevated temperature is effectually important. The kind of electrolysis solution used for measurement and the oxidation current value at the time of 4.65V were shown in Table 3.

[0106]The coin type cell of the <valuation method of high temperature conservation characteristic> above-mentioned was charged 4.1V, the charge and discharge of 4.2V to 3.0V were performed after preservation for seven days at 45 **, and the capacity of the cell was checked. The capacity of the cell at this time was 5mAh. The retention test of the coin type cell was continuously done about the same cell on two conditions of the conditions (it is called "aging") which save a cell for seven days at 45 ** after charging 4.1V, and the conditions (it is called "high temperature preservation") which save a cell for three days at 85 ** after charging 4.2V. The "5-mA service capacity" of the cell in preservation order was measured, after that a "service capacity ratio" was computed, and the high temperature conservation characteristic was evaluated from the result. The kind of electrolysis solution used for measurement and the evaluation result of the high temperature conservation characteristic were shown in Table 4. The 5-mA service capacity after preservation (after aging or high temperature preservation) was expressed with the ratio to the 5-mA service capacity at the time of un-saving, and the "service capacity ratio" made it the service capacity ratio after aging, and the service capacity ratio after high temperature preservation, respectively.

Service capacity ratio = (C/D) x100 (%)

the 5-mA service capacity at the time of 5-mA service capacity D= un-saving after C= preservation -- here, the "5-mA service capacity" of a cell is the service capacity at the time of making a coin type cell discharge with 5-mA current after charging 4.2V.

[0107]<Result> [Table 2]

	使用した電解液	過充電時のガス発生量 (m l)
実施例 1	電解液 4	0. 7 3
実施例 2	電解液 5	0. 9 0
実施例 3	電解液 6	1. 0 0
実施例 4	電解液 7	1. 1 0
比較例 1	電解液 1	0. 3 6
比較例 2	電解液 2	0. 6 2
比較例 3	電解液 1 5	0. 7 5

[0108]

[Table 3]

	使用した電解液	80°C、4.65Vの電流値 (mA/cm²)
実施例 5	電解液 3	9
実施例 6	電解液 4	1 2
実施例 7	電解液 5	1 5
実施例 8	電解液 6	2 2
実施例 9	電解液 7	1 0
比較例 4	電解液 1	0. 1 以下
比較例 5	電解液 2	5
比較例 6	電解液 1 6	5 0

[0109]the aromatic hydrocarbon compound (biphenyl.) which consists only of a fluorine atom substituted aromatic compound (2-fluorobiphenyl) and a carbon atom, and a hydrogen atom from the result of Table 2 and 3 The electrolysis solution which added both the compounds of cyclohexylbenzene became, and the oxidation current value became [the gas yield at the time of overcharge / many / (embodiments 1-4)] highly substantially rather than the fluorine atom substituted aromatic compound independent case (comparative example 5) (embodiments 5-9). Therefore, if this electrolysis solution is applied to the cell provided with the mechanism which is interlocked with the pressure in a cell and suspends charge, it shows that the cell which improved the safety at the time of overcharge is obtained.

[0110]When it experimented in Embodiments 1-3 within the calorimeter (SETARAMU C-80) and the calorific value from a cell was measured, it checked that many generation of heat had taken place rather than the electrolysis solution (comparative example 1) which does not contain an additive agent. Therefore, if especially this electrolysis solution is applied to the cell which has a mechanism which is interlocked with the temperature in a cell and suspends charge, it improves the safety at the time of overcharge, and shows that a cell with small degradation at the time of high temperature preservation is obtained.

[0111]

[Table 4]

	使用した電解液	放電容量比 (%)	
		エーシング後	高温保存後
実施例 10	電解液 5	9.4	5.2
実施例 11	電解液 6	9.4	4.5
実施例 12	電解液 7	9.4	6.0
実施例 13	電解液 8	9.6	7.3
実施例 14	電解液 9	9.4	7.3
実施例 15	電解液 10	9.6	7.5
実施例 16	電解液 11	9.7	7.4
実施例 17	電解液 12	9.4	7.5
実施例 18	電解液 13	9.7	7.2
実施例 19	電解液 14	9.7	7.4
実施例 20	電解液 15	9.6	6.8
比較例 7	電解液 1	9.1	7.2
比較例 8	電解液 2	9.3	6.8
比較例 9	電解液 16	9.3	1.0
比較例 10	電解液 17	9.8	1.1
比較例 11	電解液 18	9.5	1
比較例 12	電解液 19	9.6	5.4

[0112]The electrolysis solution (embodiments 10, 11, and 12) which contains both the compounds of the aromatic hydrocarbon compound which consists only of a fluorine atom substituted aromatic compound and a carbon atom, and a hydrogen atom from the result of Table 4, Compared with the electrolysis solution (comparative example 8) which added only the fluorine atom substituted aromatic compound, it turns out that the fall of a high temperature conservation characteristic is suppressed to the minimum. On the other hand, as for the electrolysis solution (comparative example 9) containing only the aromatic hydrocarbon compound which consists only of a carbon atom and a hydrogen atom, the high temperature conservation characteristic deteriorated substantially.

[0113]The high temperature conservation characteristic of the electrolysis solution (embodiments 13-20) which added the above-mentioned "other compounds" further is improving further.

Even if compared with the electrolysis solution (comparative example 7) which does not contain a overcharge inhibitor, the outstanding high temperature conservation characteristic was shown.

On the other hand, the electrolysis solution in which "other compounds" was added further only in the case of the aromatic hydrocarbon compound in which a overcharge inhibitor consists only of a carbon atom and a hydrogen atom is also low (comparative example 12), or the improvement factor of a high temperature conservation characteristic has not improved at all (comparative examples 10 and 11).

[0114]

[Effect of the Invention]The nonaqueous electrolyte concerning this invention has much gas volume generated at the time of overcharge, and a high overcharge preventive effect is acquired from a lot of oxidation current flowing. It excels in the high temperature conservation characteristic from the high-temperature-preservation test result in the coin cell. Therefore, safety when the lithium secondary battery containing this nonaqueous electrolyte is overcharged is improved.

It excels also in the high temperature conservation characteristic.

If it applies to the cell provided with the mechanism which is interlocked with the internal pressure and/or temperature of a cell in this nonaqueous electrolyte, and suspends charge, a cell with high safety at the time of overcharge of a cell and small degradation at the time of high temperature preservation can be obtained.

[Translation done.]